Effect of chlorine doping on photostructural defect states in amorphous selenium films

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The effect of chlorine doping on photostructural defect states in amorphous selenium films ($\sim 100 \; \mu$m) has been studied using the thermally stimulated discharge current technique. Chlorine doping in amorphous selenium results in the shift of deep photostructural defect states C_3^+ and C_1^- to relatively shallower levels, i.e., from 1.6 and 1.7 eV in pure films to 1.4 and 1.5 eV in chlorine-doped films for electrons and holes, respectively. These effects have been explained in terms of the enhancement in the conductivity of amorphous selenium and increase in the mobility of electrons and holes on chlorine doping.

Investigations on the study of the electrical behavior/polarization mechanism in amorphous selenium (a-Se) films performed either by xerographic residual potential decay measurements[1-3] or by thermally stimulated discharge current (TSD) measurements[4-6] have shown that the buildup of residual potential in these films is primarily due to the trapping of charge carriers, i.e., electrons and holes both at the shallow and the deep photostructural/intrinsic defect states C_3^+ and C_1^-, the deep defect states, of course, playing the dominant role. Therefore, these photostructural defect levels govern[7-10] the electrical properties of a-Se in general and the xerographic and xeroradiographic properties in particular. For example, in order to enhance the x-ray sensitivity of a-Se xeroradiographic photoreceptors, the value of residual potential should decrease, i.e., the trapping of charge carriers should take place at shallower levels available in the material. In order to achieve this, we have studied the effect of chlorine doping on photostructural defect states in a-Se using the TSD technique. Indeed, we have found some new and interesting results which are reported in this letter.

Films of thickness $\sim 100 \; \mu$m of pure selenium (99.999%) and selenium doped[11] with 30 ppm chlorine were vacuum deposited onto ultrasonically cleaned aluminum substrates. These films were polarized and the TSD measurements were performed in a similar way as described earlier.[4-6] The mechanism of polarization in these films is schematically shown in Fig. 1. Here the samples were irradiated with white light from a 100-W tungsten filament lamp for about 30 min. A water filter was used to cut off the infrared radiations. The intensity of illumination was about 1000 lx. The irradiation produced reversible photostructural defects on the surface of a-Se films up to a depth of a few micrometers. These defects are assumed to be of the type C_3^+ and C_1^-, as suggested by many authors.[12-16] After the exposure the films were then charged under a corona discharge. During the dark discharge of the irradiated and positively charged a-Se films, electrons trapped in the bulk of the film thermalize and move towards the corona-charged surface, where part of them get retrapped in the photoinduced electron trap states and part of them get neutralized with the surface charge. These samples were then dark rested for about 2 h for complete neutralization of the top surface charge and polarization to take place. In negatively charged a-Se films the polarization is also achieved in a similar way as discussed above, but in this case the holes would be the trapped charge carriers.

Figure 2 shows the TSD spectra of pure (curve A) and chlorine-doped (curve B) a-Se films ($\sim 100 \; \mu$m) polarized by positive charging as described above. It is seen from Fig. 2 that pure a-Se films (curve A) show two relaxation peaks designated as peaks I and II, respectively, at 310 and 374 K, whereas chlorine-doped a-Se films show (curve B) only one relaxation peak, i.e., peak II at 359 K. The negatively charged films also show similar results as is seen from Fig. 3. Here in pure a-Se films (curve C) peaks I and II are observed at 310 and 379 K, respectively, whereas in chlorine-doped a-Se films (curve D) peak I appears at 364 K. The activation energies of peak II of curves A, B, C, and D of Figs. 2 and 3 have been calculated using the initial rise method, i.e., plotting $\log I$-vs-T^{-1} plots. Such plots are shown as curves A, B, C, and D, respectively, in Fig. 4. The activation energies calculated from the slopes of these plots have been found to be 1.6, 1.4, 1.7, and 1.5 eV, respectively. It may be mentioned here from the above observations that in chlorine-doped a-Se films, as compared to pure films, there is a decrease in the peak temperature and activation energy of peak II in both positively and negatively charged films.
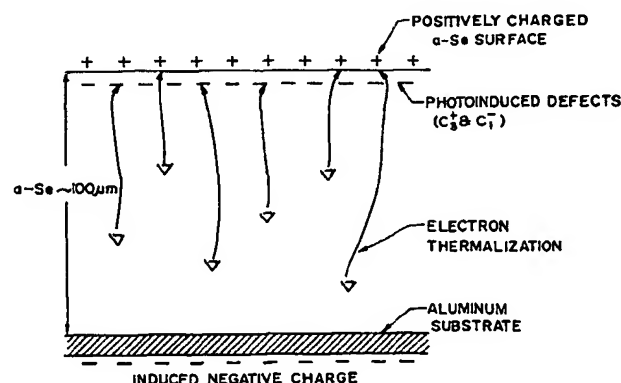

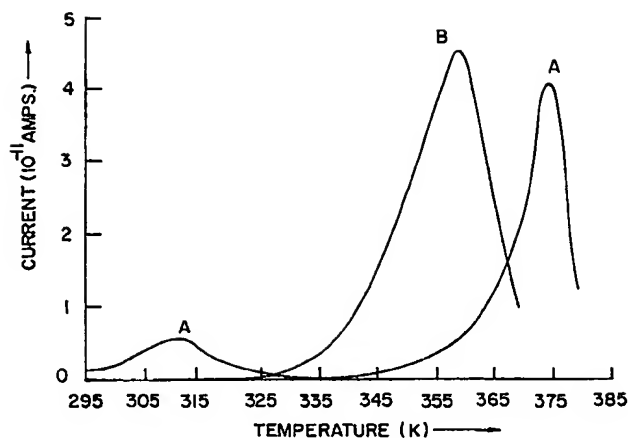FIG. 1. Mechanism of polarization in amorphous selenium films.

FIG. 4. log I-vs-T^{-1} plots for evaluation of activation energies of relaxation peaks.

FIG. 2. TSD spectra of positively charged pure (curve A) and chlorine-doped (curve B) a-Se films (~ 100 μm).

The origin of peak II in a-Se films has been attributed[6] to the trapping of charge carriers at deep photostructural/intrinsic defect levels lying at 1.6 and 1.7 eV for electrons and holes, respectively. These photostructural defect states, which are assumed to be of the type C_3^+ and C_1^- and arise due to the dangling bonds of the broken selenium chains, are the primary source of trapping for electrons and holes, respectively, in a-Se films, as suggested by various other authors.[12-16] Further in amorphous materials like selenium these charge trapping states exist[17] at the grain boundaries, i.e., amorphous/crystalline regions. The doped chlorine perhaps goes into these regions and introduces conducting paths at these grains, thus increasing the conductivity and reducing the barrier at the grains. The shift in the peak temperature of peak II and a decrease in its activation energy on chlorine doping supports the above conductivity enhancement role of chlorine in a-Se. It indicates the in-
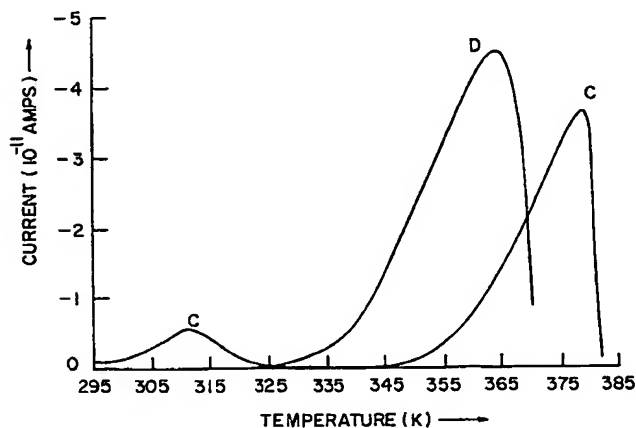
crease in the mobility of the charge carriers, i.e., both electrons and holes and their trapping at relatively shallower levels during polarization. This suggested mechanism finds further support from observations of other authors[3,11] who, based on the investigations of the electrical properties of a-Se films in the electrophotographic mode, found that chlorine doping in these films results in the increase in the thermal generation rate of the charge carriers, the decrease in the resistivity of the material, i.e., the decrease in the imaging/acceptance potential of the films, etc.

In conclusion, it may be suggested that chlorine doping in a-Se affects both the electrons and hole trapping levels. It results in the increase in the mobility of both electrons and holes and also a shift in the deep photostructural/intrinsic defect states to the relatively shallower levels as compared to the corresponding states in pure amorphous selenium films.

FIG. 3. TSD spectra of negatively charged pure (curve C) and chlorine-doped (curve D) a-Se films (~ 100 μm).

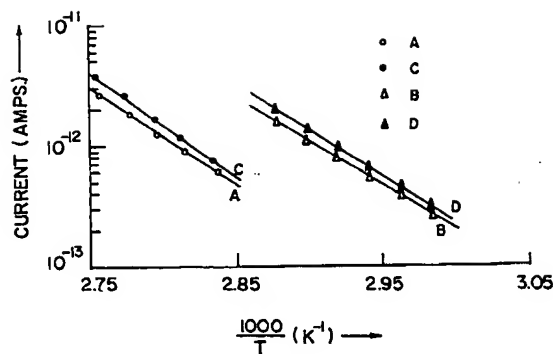[1] M. Abkowitz and R. C. Enck, Phys Rev. B 25, 2567 (1982).
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